

**MICROFIBRILLATED CELLULOSE COMPOSITION HAVING
EXCELLENT REDispersing AND SUSPENDING PROPERTY**

11-W1115-03

Patent number: JP60186548
Publication date: 1985-09-24
Inventor: FUKUI KATSUTADA; others: 01
Applicant: DAICEL KAGAKU KOGYO KK
Classification:
- international: C08L1/00
- european:
Application number: JP19840042362 19840306
Priority number(s):

Abstract of JP60186548

PURPOSE: To provide the titled composition having excellent redispersing and suspending property in water to give a highly viscous dispersion, by adding a specific water-soluble substance to an aqueous suspension of microfibrillated cellulose, and dehydrating the mixture.

CONSTITUTION: An aqueous suspension of microfibrillated cellulose is added with ≥ 10 wt% water-soluble substance, especially a carbohydrate (e.g. glucose, sucrose, etc.) based on the solid component of the cellulose. The mixture is dehydrated and dried to obtain the objective composition having a stability index of ≥ 0.9 .

Data supplied from the **esp@cenet** database - Patent Abstracts of Japan

THIS PAGE BLANK (USPTO)

⑨ 日本国特許庁(JP)

⑩ 特許出願公開

⑫ 公開特許公報(A)

昭60-186548

⑤ Int.Cl.⁴

識別記号

庁内整理番号

④ 公開 昭和60年(1985)9月24日

C 08 L 1/00

6958-4J

審査請求 未請求 発明の数 1 (全3頁)

⑬ 発明の名称 再分散懸濁性の良好なマイクロファイブリル化セルロース組成物

⑭ 特 願 昭59-42362

⑮ 出 願 昭59(1984)3月6日

⑯ 発 明 者 福 井 克 任 姫路市網干区新在家940

⑰ 発 明 者 仲 田 勝 晴 姫路市網干区新在家940

⑱ 出 願 人 ダイセル化学工業株式 堺市鉄砲町1番地
会社

明 細 書

1. 発明の名称

再分散懸濁性の良好なマイクロファイブリル化セルロース組成物

2. 特許請求の範囲

(1) マイクロファイブリル化セルロースの水懸濁液に、そのセルロース固形分重量の10重量%以上の水溶性物質を添加混合し、脱水してなる組成物であつて、本文に定義する安定性指標が0.9以上であるマイクロファイブリル化セルロース組成物。

(2) 水溶性物質が炭水化物である特許請求範囲第1項記載のマイクロファイブリル化セルロース組成物。

3. 発明の詳細な説明

本発明は、一旦脱水した後も、再度水に投した際に良好な再分散懸濁性を示すマイクロファイブリル化セルロース組成物に関するものである。

マイクロファイブリル化セルロース(以下MFCと略す)は、パルプを特開昭56-100801号

明細書に示された方法により、水中で粘状叩解して得られるもので、セルロース繊維の結晶構造を物理的に破壊し、微細ファイブリル化したものである。上記明細書には、「微小繊維状セルロース」として定義されている。このMFCは非常に大きな水保持力、水中での安定な分散懸濁性、各種化学試薬酵素類に対する高い反応性などで特有の性質があり、広汎な用途が期待される。

しかしながら、MFCは、固型分濃度が6%以下の水懸濁液の状態で製造されるので、これをそのまま保存、あるいは輸送すると種々の問題が起こる。即ち水含量が大きいため輸送などに不便であり、化学反応性の高い状態のものが水に懸濁しているため、微生物による腐敗現象も起こりやすい。また用途によつては、大量の水の同伴は好ましくない場合も多い。

生物化学反応による品質低下を防止する方法の最も一般的なのは、素材を脱水乾燥することである。MFCにおいても、これを水懸濁液の状態から脱水し、乾燥することによつて保存、安定性

に優れたものとする事は可能である。しかしながらMFCの場合水を含有する状態から乾燥する過程で、品質的に変化が生じてしまい、凝集してしまう。これはMFCの水酸基による水素結合の作用と考えられ、乾燥したMFCを水中に投じても、これは容易に再分散しないので、もとのような均一な水懸濁液とするのは甚だ困難である。

一般に乾燥した物の再懸濁性は、その乾燥工程に、依存する。即ち、加熱乾燥、減圧加熱乾燥、凍結乾燥などの乾燥手段において、凍結乾燥が最も乾燥工程における品質の変化が少ない方法として知られている。MFCの場合は、凍結乾燥をできるだけ固形分濃度の低い懸濁液(例えば0.5%以下)から出発して行つたものに強力な機械的攪拌を加えてやることにより、再分散をすることを認めたが、その場合でも、再懸濁されたMFCは、乾燥処理前のMFCに比べ、保水性、分散安定性、高粘性などの物性に劣るものしか得られない。

特開昭58-206601号明細書には、再分散懸濁手段として超音波照射が有効であることが示

されており、その他強力なホモジナイザー等による強い攪拌も有効であるが、これらは、特別な装置を必要とするため、商品流通過程での問題を解決するには至らない。

本発明者等は、特別な装置を用いることなく、一旦脱水乾燥しても通常の混合攪拌機で容易に水に再分散できるような性質を付与する技術について鋭意研究した結果、MFCの水懸濁液に、水溶性物質を添加混合し、脱水して得られる組成物が、乾燥後も容易に水に再分散し、高粘性を示すことを認め本発明に到達した。

本発明に使用する水溶性物質とは、常温で固体である物質が好ましく、特に炭水化物が適当である。例示すれば、グルコース、しよ糖、でんぷん、デキストリン、ペクチン、ローカストビーンガム、アラビアガム、カラギーナン、カルボキシメチルセルロース、ヒドロキシエチルセルロースなどであり、単糖類、多糖類及び多糖類の水溶性誘導体を含む。

本発明に使用する水溶性物質の量は、MFCに

対しその乾燥重量比で10%以上の割合で混合するのが望ましく、組成物の乾燥後の水への再分散を容易にする。また、水溶性物質の添加量の上限は、実用的な見地にもとづくものであり、MFC乾燥重量の3倍量以下が適当である。水溶性物質として、しよ糖、デキストリンなどの天然物乃至食品添加物を使用すれば、得られる組成物もまた、食品添加用に使用することができる。

本発明の組成物は、MFCの水懸濁液に比べ、輸送、包装費が節減でき、菌の繁殖などによる変質の防止などの効果が期待される。

以下に実施例をあげて本発明を説明する。
尚安定性指標の求め方は次の通りである。

MFCを含む組成物に水を加えてセルロース固形分濃度0.5%となるよう調整し、ホモミキサーで1000rpm、1分間攪拌後メスリンダーに移し、室温で1分間静置した後、全容量に対する分散懸濁量(上澄み層を除いた容量)を求め、安定性指標とする。(尚本実験に使用したホモミキサーは東洋理化学材料製ハイスターH1-25

である。)

比較例

セルロース固形分濃度2%のMFC懸濁液(粘度6020cps, 25℃ B型粘度計)を105℃ 6時間処理して乾燥MFCを得た。乾燥MFCに固形分2%濃度となるよう計算量の水を加えてホモミキサーで攪拌し、懸濁分散液を作製した。この懸濁分散液の粘度は10cps以下(2%)、安定性指標は0.025(0.5%)であつた。

実施例1

比較例に用いたと同じMFC懸濁液100gにしよ糖の2%水溶液100gを加えて攪拌混合し、セルロース固形分濃度1%(全固形分濃度2%)の懸濁液を得た。懸濁液を105℃で6時間乾燥し、乾燥組成物をえた。乾燥組成物をホモミキサーを用いて水に再分散懸濁したところ安定な懸濁液を得た。

原懸濁液の粘度1270cps、乾燥組成物の再懸濁液(セルロース固形分濃度1%)の粘度1460cps、安定性指標(0.5%)1.0を得た。即ち、

乾燥組成物の再分散懸濁安定性、増粘性など良好なものであつた。

実施例 2.

実施例 1 のしよ糖の代りにキサンタンガム（エコーガムケトロール、大日本製薬）を用いて同様の実験を行つた。

原懸濁液の粘度 1810 cps，乾燥組成物の再懸濁液の粘度 1700 cps，安定性指標 1.0 であつた。

実施例 3.

実施例 1 のしよ糖の代りにデキストリン（バインデックス、松谷化学）を用いて、同様の実験を行つた。

原懸濁液の粘度 1520 cps，乾燥組成物の再懸濁液の粘度 1420 cps，安定性指標 1.0 であつた。

特許出願人 ダイセル化学工業株式会社

THIS PAGE BLANK (USPTO)

Article

Effect of Fiber Concentration and Axial Ratio on the Rheological Properties of Cellulose Fiber Suspensions

Daisuke TATSUMI, Satoshi ISHIOKA, and Takayoshi MATSUMOTO*

*Division of Forest and Biomaterials Science, Graduate School of Agriculture,
Kyoto University, Kyoto 606-8502, Japan
(Received: September 28, 2001)*

The steady flow and the dynamic viscoelastic properties of cellulose fiber suspensions were investigated as functions of the suspension concentration and the fiber shape using a parallel-plate type rheometer. Various concentrations of the suspensions were made from various types of cellulose fibers, i.e., microcrystalline cellulose, bacterial cellulose, and fibrillated cellulose fibers. All the suspensions showed non-Newtonian flow even at very low concentrations. The flow property of each suspension showed a plateau of the shear stress, i.e., the yield stress, over a critical concentration. The critical concentration obtained from the experiment agreed well with the value theoretically calculated from the axial ratio of the fibers. The dynamic moduli of the suspensions were almost independent of the angular frequency, and they increased with the fiber concentration. The dynamic storage moduli increased in proportion to the 9/4th power of the fiber concentration. This power of 9/4 is coincident with that theoretically required for polymer gels. This fact suggests that the rigidity of the suspensions has appeared by the same mechanism from the order of cellulose fibers to microcrystalline cellulose fibers, and even to polymer molecules.

Key Words: Cellulose fibers / Suspensions / Axial ratio / Rheology / Power law

1. INTRODUCTION

Fiber suspensions generally have remarkably higher viscosity and elasticity than spherical particle suspensions of equal volume concentration. It makes them hard to deal with in various industrial fields. For example, in the paper industry, the viscosity of the pulp fiber suspension is controlled by maintaining very low fiber concentration around 1% in order to make the suspension flow uniformly. However, such a low concentration is disadvantageous for energy and water consumption. Therefore, further efficiency improvement has been required to control such characteristics of the fiber suspensions.

Many researchers have made efforts to clarify the characteristics of the fiber suspensions. Mason¹⁾ paid attention to the large excluded volume of a fiber. He proposed the following equation for the critical concentration, c_0 , at which fibers are no longer able to undergo free rotation:

$$c_0 = V_a/V_e = 3/(2p^2) \quad (1)$$

where V_a is the actual volume of a fiber, V_e is the effective volume swept out by a rotating fiber and is equal to that of a sphere whose diameter equals the fiber length, and p is the

axial ratio (length/diameter) of the fiber. When the concentration of a suspension is over c_0 , the effect of the fiber network structure due to the fiber-fiber interaction becomes important. Some researchers have measured the fiber network strength using simple tensile tests for solidified cellulose suspensions.^{2,3)} Kerekes *et al.*⁴⁾ summarized these experimental results in a simple power equation:

$$\sigma_y = kc_m^\alpha \quad (2)$$

where σ_y is the yield stress of the suspension, c_m is the mass concentration of the suspension, and k and α are constants. They have reported that the constants are unique for every suspension and the values are in the intervals of $1.18 < k < 24.5$ and $1.26 < \alpha < 3.02$, respectively. Bennington *et al.*⁵⁾ have extended the equation theoretically:

$$\sigma_y = k' E p^2 c_v^3 \quad (3)$$

where c_v is the volumetric concentration of the suspension and E is Young's modulus of the fiber. However, they found that this equation does not agree with their experimental results as to the powers of E and p .

Recently, many researchers have measured the fiber network strength using disruptive shear tests.⁶⁻⁸⁾ However,

THIS PAGE BLANK (USPTO)

there have been few investigations that deal with a rotational rheometer systematically. In a previous study,⁹⁾ we investigated the effect of the fiber concentrations on the rheological properties of the cellulose fiber suspensions. In the present study, we investigated the effect of not only the fiber concentrations but also the axial ratio of the fiber on the rheological properties of the suspensions. We also examined what the constants k and α depend on. The relationships between the moduli of the suspension and the fiber concentration were observed and discussed.

2. EXPERIMENTAL

2.1 Materials

One of the cellulose fibers used in this study was made in our laboratory by hydrolysis of the cotton cellulose Whatman® CF11. It was prepared by treating 10 g of CF11 with 200 ml of 4N hydrochloric acid at 80°C for 225 min.¹⁰⁾ It was repeatedly washed with centrifugation and then dialyzed with distilled water until the electrical conductivity of the outer liquid became equal to that of distilled water. This takes almost a month. An ultrasonic treatment is required to refine the

hydrolyzed CF11. The treatment was done with an ultrasonic disrupter (UD-200, Tomy Seiko Co., Ltd., Japan) for 1 hour at a frequency of 20 kHz, and the microcrystalline cellulose fiber obtained was named CF11H. Another fiber sample was a commercial product Ceolus® FP-3, kindly supplied by Asahi Kasei Corporation, Japan. Bacterial cellulose (BC) used in this study was kindly supplied by Bio-Polymer Research Co., Ltd., Japan. A part of it was hydrolyzed, centrifuged, and purified by dialysis as described above, and it was called BCH. Celish® KY-100G, microfibrillated cellulose made from purified wood pulp, kindly supplied by Dical Chemical Industries, Ltd., Japan, was also used. Before measurements, all the cellulose fibers were dispersed in distilled water to a required concentration and then treated by the ultrasonic disrupter for 5 min in order to disperse them thoroughly.

The cellulose fibers were observed with a scanning electron microscope (SEM: JSM-T330A, JEOL, Ltd., Japan) or an atomic force microscope (AFM: NV2000, Olympus Optical Co., Ltd., Japan), as shown in Fig. 1. The average lengths L and diameters D of the fibers are shown in Table I with the calculated axial ratios p . The diameter of BC was not changed by the hydrolysis.

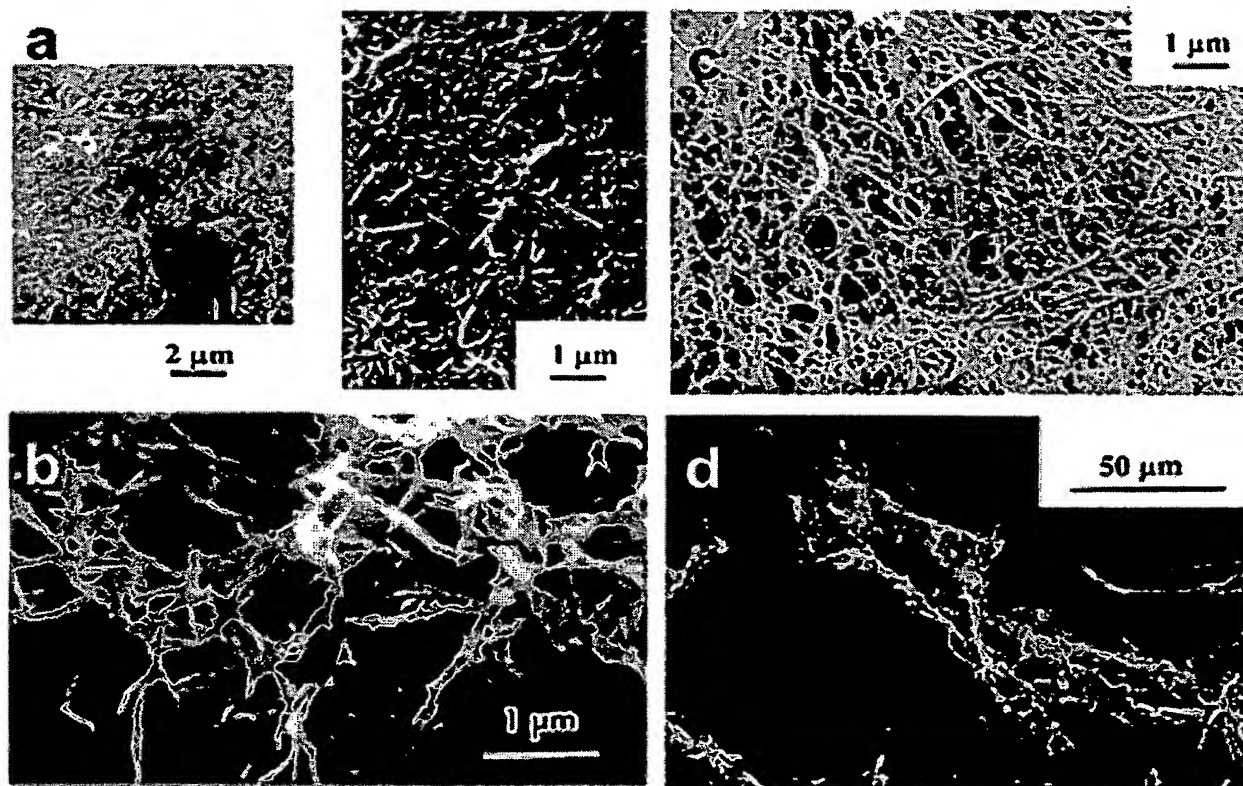


Fig.1 SEM Micrographs of cellulose fibers; a: Hydrolyzed CF11 (i.e., CF11H), the left side is an AFM image, b: Ceolus, c: Bacterial cellulose, d: Celish.

THIS PAGE BLANK (USPTO)

Table I The average sizes of cellulose fibers

Fiber	$L / \mu\text{m}$	$D / \mu\text{m}$	p
CF11H	0.72	0.017	42
Ceolus	1.7	0.077	22
BC	6–12	0.027	220–450
BCH	2.2	0.027	81
Celish	350	15	25

2.2 Measurements

The rheological properties were measured with a parallel-plates type rheometer (Rhosol-G2000, UBM Co., Ltd., Japan) devised to prevent vaporization of water. The diameters of the plates were 50 mm. All the measurements were performed at 30°C with varying fiber concentrations of the suspensions. The data were collected from low to high shear condition to avoid disrupting the suspension structure. The dynamic strain amplitude was 0.05, at which all the samples showed linear viscoelasticity. The fibers tend to aggregate gradually during the measurement, so that the measurements were carried out soon after the sample preparations.

3. RESULTS

3.1 Flow properties

The flow properties of the cellulose suspensions were examined by steady flow measurements. The gap between the plates of the rheometer should be sufficiently larger than the fiber length.¹¹⁾ We first examined the gap dependence of the measurements. Figure 2 shows logarithmic plots of the shear stress, σ , versus shear rate, $\dot{\gamma}$, for the Celish suspensions at a concentration of 0.3 wt%. When the gap was less than 1.0 mm, the flow curves depended on the gap and varied complicatedly. On the other hand, when the gap was 1.5 or 2.0 mm, the curve was smooth and the reproducibility was good. Therefore, a gap of 1.5 mm was selected for the following measurement of the Celish suspension. For the other fiber suspensions, there were no significant gap dependences. Even when the gap was as narrow as 0.5 mm, the measured flow curve was coincident with that measured using a cone-plate fixture. The gap was determined to be 1.0 mm for the measurement of the fiber suspensions except the Celish one.

Figure 3 shows the flow properties for the CF11H suspensions at various concentrations from 0 to 3.0 wt%. The 0 wt%, i.e., water, and the 0.1 wt% suspensions showed Newtonian flows. However, when the concentrations became higher than 0.3 wt%, the suspensions showed noticeably non-Newtonian flows. That is, the flow curves became flat for the abscissa. The values of the shear stress in the plateau region,

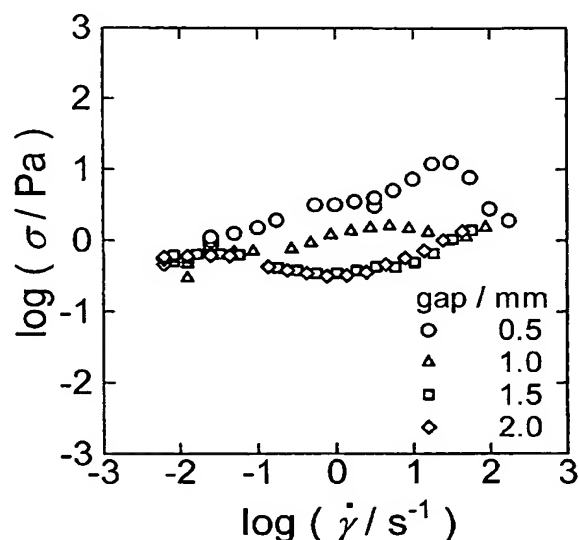
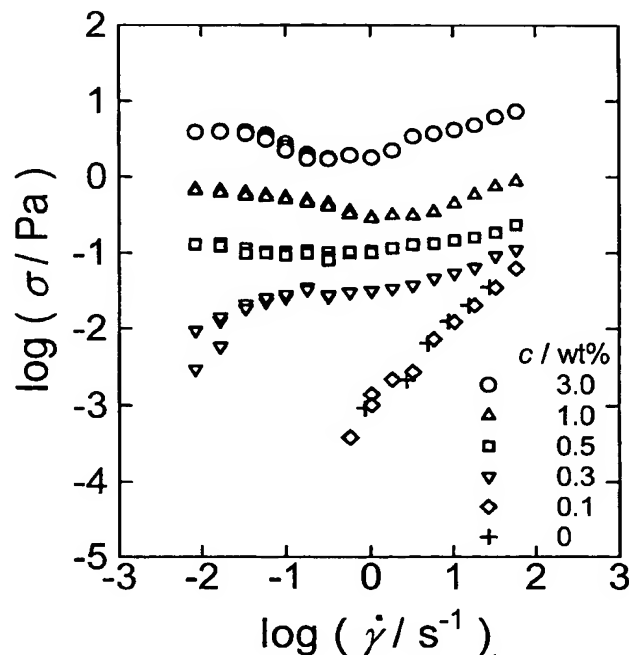


Fig.2 Effect of gap between plates on the flow curve of 0.3 wt% Celish suspension.

Fig.3 Logarithmic plots of shear stress, σ , versus shear rate, $\dot{\gamma}$, for various CF11H suspension concentrations, c .

which is designated as the yield stress, σ_y , of the suspension, increased with the fiber concentration. Figures 4 and 5 show the flow curves of the Celish and the BC suspensions. Although Celish is much larger than the other fibers, it does not sediment because of its microfibrillated surface. The flow curves of the Celish suspensions were very similar to those of the CF11H ones. On the contrary, the flow curves of the BC

THIS PAGE BLANK (USPTO,

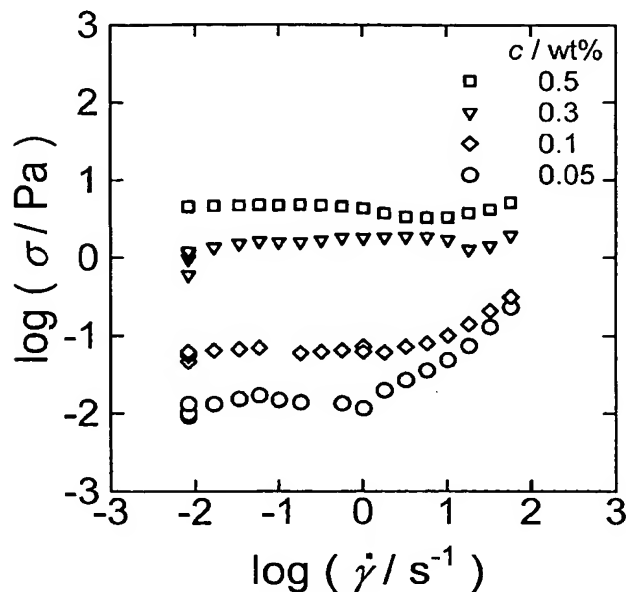


Fig. 4 Logarithmic plots of shear stress, σ , versus shear rate, $\dot{\gamma}$, for various Celish suspension concentrations, c .

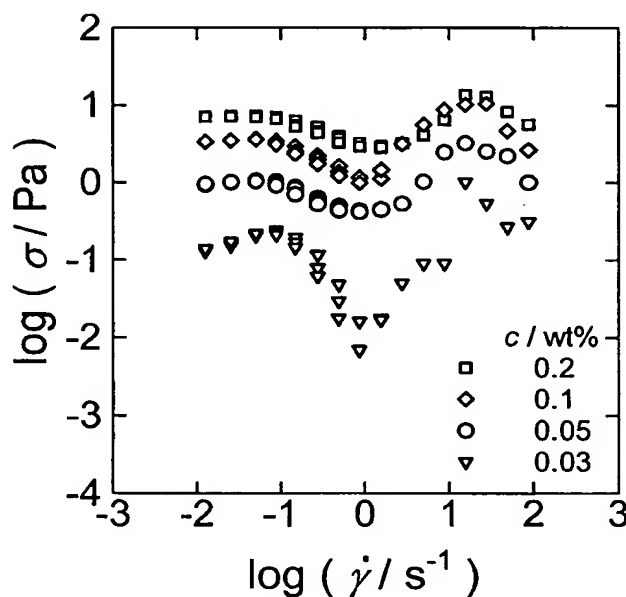


Fig. 5 Logarithmic plots of shear stress, σ , versus shear rate, $\dot{\gamma}$, for various BC suspension concentrations, c .

suspensions were quite unique. There were stress drops in the middle $\dot{\gamma}$ region. The drops were noticeable at the low concentration. However, the tendency for the yield stress to increase with the fiber concentration was the same as that of the other fiber suspensions.

The yield stresses, σ_y , at $\dot{\gamma} = 0.01 \text{ s}^{-1}$ were logarithmically plotted versus the fiber concentrations, c , for all the suspensions and are shown in Fig. 6. A power law relationship

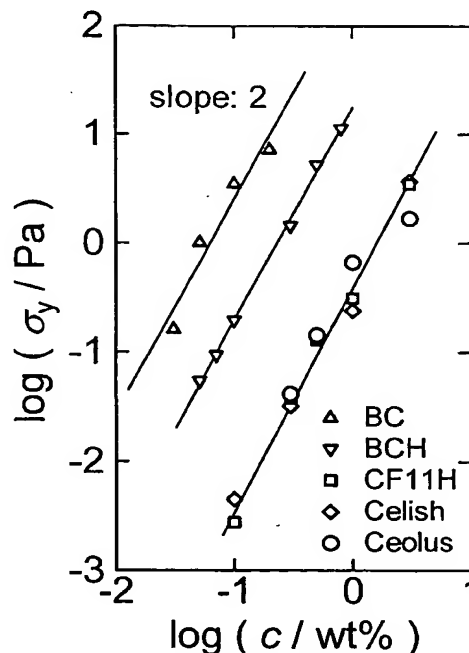


Fig. 6 Logarithmic plots of yield stress, σ_y , versus fiber concentrations, c , for various fiber suspensions. $\dot{\gamma} = 0.01 \text{ s}^{-1}$.

with a power of 2 was fitted to the experimental data for all the suspensions. The BC suspension had the highest σ_y value in the measured sample at a certain concentration. The value became about one-tenth that of the original BC's due to the acid hydrolysis. The plots for CF11H, Celish, and Ceolus lay on a single line in spite of the variation in their size.

3.2 Dynamic viscoelasticity

The dynamic storage moduli, G' , and the loss moduli, G'' , plotted against the angular frequency, ω , for the CF11H suspensions are shown in Fig. 7. The moduli were almost independent of ω at any fiber concentration. The G' values were about ten times that of G'' at the same concentration. They increased with the fiber concentration. The other fiber suspensions demonstrated almost the same rheological properties as the CF11H suspension. The plateau levels of the moduli, G' and G'' , at $\omega = 0.01 \text{ s}^{-1}$ were plotted against the fiber concentrations, c , for various cellulose suspensions as shown in Fig. 8. The result is very similar to the plots of σ_y versus c shown in Fig. 6. The moduli became smaller in the order, the BC, the BCH, and the other fiber suspensions, at a certain concentration. A single line was fitted to the data for the CF11H, the Celish, and the Ceolus suspensions. The moduli increased in proportion to $c^{9/4}$, regardless of the types of the fibers.

THIS PAGE BLANK (USPTO)

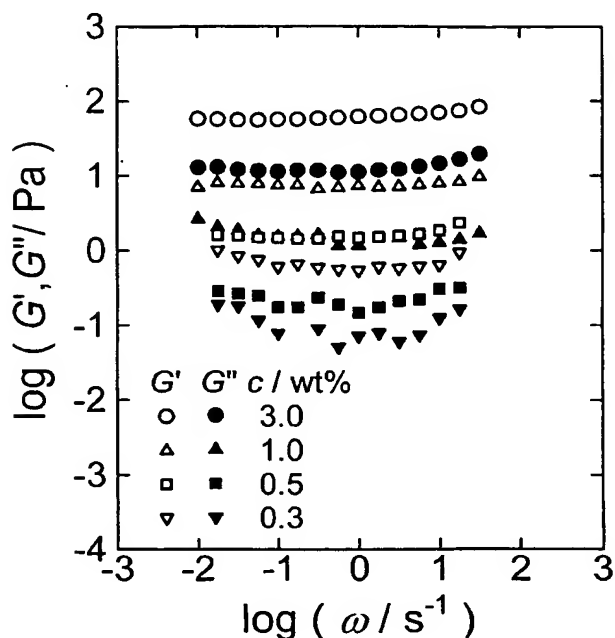


Fig. 7 Logarithmic plots of dynamic storage moduli, G' , and dynamic loss moduli, G'' , versus angular frequency, ω , for various CF11H suspension concentrations, c .

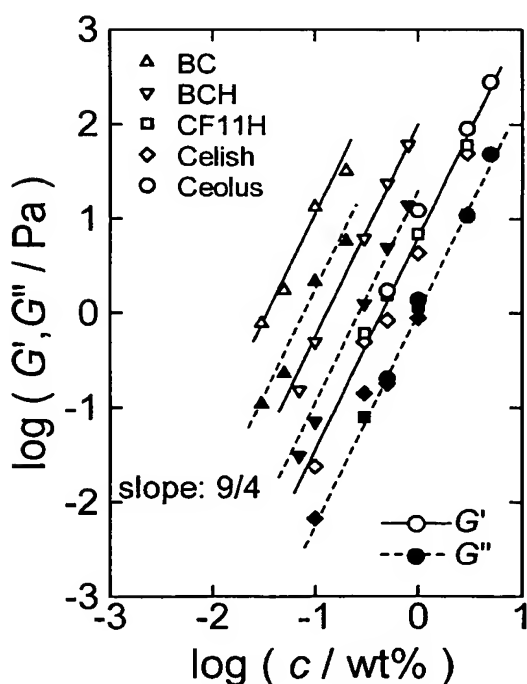


Fig. 8 Logarithmic plots of dynamic moduli, G' and G'' , versus fiber concentrations, c , for various fiber suspensions. $\omega = 0.01 \text{ s}^{-1}$.

4. DISCUSSION

The concentration at which the flow behavior of a suspension shifts to a non-Newtonian from a Newtonian flow is considered as the critical concentration. The concentration of 0.3 wt% for the CF11H suspension was compared with c_0 calculated from Eq.(1). Using the axial ratio of the fiber listed in Table I, we obtained the critical concentration, c_0 , of 0.3 wt%. The calculated value agreed well with that evaluated by the rheological measurement. For the other microcrystalline cellulose suspensions (the Ceolus⁹⁾ and the BCH suspensions), c_0 calculated from Eq.(1) also agreed well with the experimental results. The fact indicates that Mason's estimation¹⁾ can be applied to the microcrystalline cellulose fiber suspensions.

Fibers have a larger excluded volume than spherical particles. Therefore, the interaction between fibers is strong even at the low fiber suspension concentration. This is more remarkable as the fiber axial ratio becomes larger. In this case, the fibers tend to form flocs rather than remaining individual fibers because the former is more stable thermodynamically. The stress drops of the BC suspension in Fig.5 were thus considered to be derived from flocculation of the fibers. In practice, we observed the small flocs of the BC fibers after the steady flow measurement.

The plateaus of σ_y shown in Figs.3, 4, and 5 indicate that some network structures consisting of individual fibers were formed in the suspensions. The dynamic storage moduli of the suspensions also had plateaus as shown in Fig.7. It can be said that each suspension has a solid-like structure even at such low concentrations.

A power law relation was fitted to the data of σ_y versus c in Fig.6. The results almost agree with the earlier study.⁴⁾ This indicates that Eq.(2) can be applied over a wide range of fiber length and diameter. The power of 2 indicates that the origin of the yield stress is a two-body collision.

The other power law was also fitted to the dynamic data in Fig.8. The plots for the CF11H, the Celish, and the Ceolus suspensions lay on a single line. Their axial ratios, p , are almost the same, though their length and diameter differ from each other as shown in Table I. The moduli increased with p , so that the moduli are considered to be a function of p . Because the yield stress is related to G' , σ_y is also a function of p . Thus, the factor, k , in Eq.(2) is expressed by p , i.e., $k = k(p)$. Comparing Eq.(2) with Eq.(3), k is assumed to be in proportion to p^2 . By using the power relations between G' and c in Fig.8, the k values can be estimated, considering that G' is

THIS PAGE BLANK (USPTO)

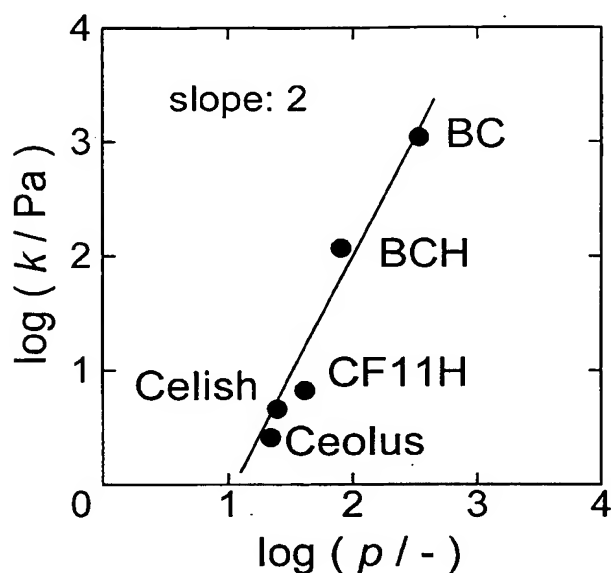


Fig.9 Logarithmic plots of the factor, k , versus axial ratio of fibers, p .

expressed as $G' = kc^\alpha$. The values for the BC, the BCH, the CF11H, the Celish, and the Ceolus suspensions are 1080, 120, 6.7, 4.6, and 2.6 Pa, respectively, when c is expressed by wt%.

The obtained k values were logarithmically plotted against the axial ratio, p , as shown in Fig.9. The result indicates that the k values are almost proportional to the square of the axial ratio of each fiber as we expected above. This fact suggests that k reflects individual fiber characteristics such as the axial ratio and Young's modulus of a fiber. On the contrary, the exponent value, α , did not change in spite of the variation in the fiber types as shown in Fig.8. This fact suggests that α does not reflect the individual characteristics of the fibers but the structural property of the whole suspension. The power agrees well with previous studies for that of pulp fiber suspensions.^{11,12)} In addition, the power of 9/4 is consistent with that for polymer gels in a good solvent according to the scaling theory.¹³⁾ This fact indicates that the rigidity of the fiber suspensions has appeared by the same mechanism from the order of cellulose fibers to microcrystalline cellulose fibers, even to polymer molecules.

5. CONCLUSIONS

The cellulose fiber suspensions show the yield stress, σ_y , and the pseudo-equilibrium modulus even at very low concentrations. A power law correlation was found between the moduli, G' , and the concentrations, c , of the suspensions, i.e., $G' = kc^\alpha$. The factor, k , changed with the types of the fibers, so that the k value reflects the individual fiber characteristics. On the other hand, the power, α , was constant around 9/4 over a wide range of fiber length and diameter, regardless of the types of fibers. This indicates that α reflects the structural property of the whole suspension.

REFERENCES

- 1) Mason SG, *Pulp Paper Mag Can* 51, 94 (1950).
- 2) Forgacs OL, Robertson AA, Mason SG, "Fundamentals of Papermaking Fibres", Bolam F ed, (1958), Technical Section of the British Paper and Board Makers' Association, Kenley, p447.
- 3) Reeves DC, Gerischer GFR, *Appita* 35, 316 (1982).
- 4) Kerekes RJ, Soszynski RM, Tam Doo PA, "Papermaking Raw Materials", Punton V ed, (1985), Mechanical Engineering Publications Limited, London, p265.
- 5) Bennington CPJ, Kerekes RJ, Grace JR, *Can J Chem Eng* 68, 748 (1990).
- 6) Bennington CPJ, Kerekes RJ, Grace JR, *Can J Chem Eng* 69, 251 (1991).
- 7) Bennington CPJ, Azevedo G, John DA, Birt SM, Wolgast BH, *J Pulp Paper Sci* 21, J111 (1995).
- 8) Hietaniemi J, Gullichsen J, *J Pulp Paper Sci* 22, J469 (1996).
- 9) Tatsumi D, Ishioka S, Matsumoto T, *Nihon Reorogi Gakkaishi* 27, 243 (1999).
- 10) Araki J, Wada M, Kuga S, Okano T, *Colloid Surf A* 142, 75 (1998).
- 11) Damani R, Powell RL, Hagen N, *Can J Chem Eng* 71, 676 (1993).
- 12) Swerin A, Powell RL, Ödberg L, *Nord Pulp Paper Res J* 7, 126 (1992).
- 13) de Gennes P-G, "Scaling Concepts in Polymer Physics", (1979), Cornell University Press, Ithaca.

THIS PAGE BLANK (USPTO)

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)